

Potato Starch Factory Waste Effluents

III. Recovery of Organic Acids and Phosphate^a

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The use of anion-exchange resins for removal of acids from potato starch factory waste-water (after prior removal of proteins and amino acids) was studied. Over 99% of the acids were removed by the process. Data are given on the effect of influent temperature and flow-rate on column efficiency during the acid adsorption step. Data are also given on methods of increasing the concentration of acids in the eluate by increasing the alkalinity of the eluting agent or by recycling the eluate. Possible uses for the eluate are discussed.

1. Introduction

The liquid waste effluents of potato starch factories have an extremely high biochemical oxygen demand (b.o.d.) and therefore require an efficient type of sewage or other waste treatment. However, the potato starch industry operates on a narrow margin of profit and probably could afford added waste treatment costs only if this treatment recovered useful materials from the waste.

Previous publications from this Laboratory have discussed the reverse osmosis concentration of the effluent,¹ the recovery of protein,² the recovery of potassium and other cations,³ the laboratory-scale removal of amino compounds by cation-exchange^{4,5} and the operational data required for evaluating the commercial possibilities of the latter process.⁶ After these treatments, however, phosphoric acid and organic matter, including sugars and several organic acids, are left in the waste. It thus could still cause problems of oxygen depletion or eutrophication if allowed to flow into streams or lakes. The present paper gives data on the use of anion-exchange resins to remove the acids. It also discusses possible uses for the recovered acids and the nature of the unidentified acids present.

2. Experimental

The wastes used for this study were the effluents resulting from the amino-acid recovery step.⁶ These effluents were frozen until needed.

Ion-exchange studies were performed using water-jacketed glass-pipe columns [1-in (25.4 mm) × 48 in (1.21 m) long]^b containing 317 ml [24.3 in (≈0.617 m)] of wet

^a Part II in this series is *J. Sci. Fd Agric.* 1972, 23, 745.

^b Fischer & Porter Company. Mention of company or trade names does not imply endorsement by the Department over others not named.

resin. Two types of weak-base anion-exchange resin^a were studied—IRA-68, a standard “gel”-type resin and IRA-93, a macroreticular resin. Water from a controlled-temperature bath was circulated through the jackets. Constant-flow pumps were used for all streams—waste input, wash water and regenerant. The pH of liquids at the column outlet was continuously recorded using Corning combination electrodes set in glass flow-cells. Total acidities were determined by titrating to a phenolphthalein end-point; individual acids were determined by the ion-exchange method of Schwartz, Greenspun and Porter.⁷ The dichromate reflux method⁸ was used for estimating chemical oxygen demand (c.o.d.). Reducing sugars were determined by the Shaffer-Somogyi micro method,⁹ solids by heating at 90 °C in a forced-draft oven.

For phosphorus analysis the sample, plus 50 mg of magnesium acetate, was evaporated to dryness in a platinum dish (steam bath). After four drops of olive oil were added the sample was ashed at 600 °C for 1 h. The residue was dissolved in hot 1:4 HCl and transferred to a 100-ml volumetric flask. Phosphorus was then determined by the method of Scroggins.¹⁰ All apparatus was first rinsed with hot 1:4 HCl to remove traces of phosphorus from detergents, etc.

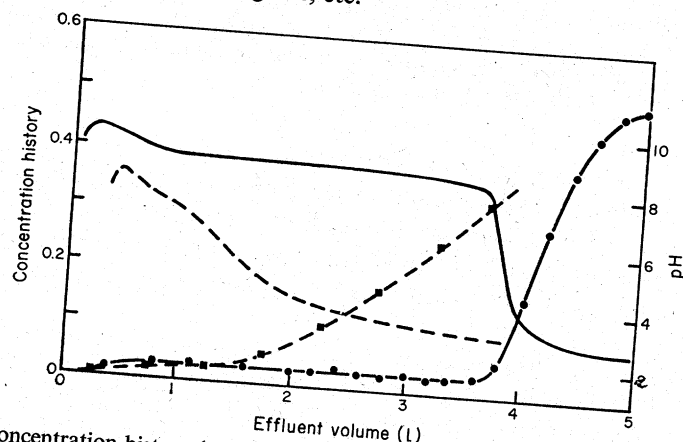


Figure 1. Concentration history (ratio of acidities, effluent to influent) and pH of anion-exchange effluents. —, pH, IRA-68; ---, pH, IRA-93; ■—■, IRA-93; ●—●, IRA-68.

3. Results and discussion

3.1. Adsorption of acids

For acid adsorption the two resins were used in the free-base form. Figure 1 shows the effluent pH and concentration history (ratio of acidities, effluent to influent) for two runs. For the run with the macroreticular resin (IRA-93) influent acidity was 0.12 mequiv./ml and flow-rate 15.1 b.v. (bed volumes)/hour. For the run with the “gel”-type resin (IRA-68) influent acidity was 0.16 mequiv./ml and flow-rate 12.0 b.v./h.

The superiority of the IRA-68 in this application is evident in the Figure. When the flow-rate for the IRA-93 was reduced from 15.1 to 7.0 b.v./h its performance, though improved, still did not meet that of the IRA-68 at 12 b.v./h. For this reason the latter was used in all further studies.

^a Kindly furnished by Rohm and Haas Company, Philadelphia, Pa.

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In the preceding runs, influents were kept at 30 °C during the adsorption step. To examine the effect of changes in influent temperature and flow-rate, a series of runs was made in groups of three—the members of each group using the same influent batch. The first run was made under conditions taken as standard—influent temperature 30 °C, flow-rate 16.2 b.v./h. For the second run the temperature was kept at 30 °C, but the flow-rate was decreased to 12.0 b.v./h; for the third the flow-rate was kept at 16.2 b.v./h., but the temperature was increased to 50 °C. Milliequivalents of acid adsorbed by the column up to the acid break-through point was taken as the measure of column efficiency. This was determined by measuring, as accurately as possible, the volume of influent put through the resin and titrating both influent and effluent. The break-through point was taken as the point where the slope of the pH curve increased to 45 °C.

TABLE 1. Effect of influent temperature and flow rate on acid adsorption

Adsorption in standard runs ^a (mequiv.)	Change in adsorption Slow flow, 12.0 b.v./h (%)	High tem- perature 50 °C (%)	Influent concentration ^b
470	+11.1	+1.0	High
468	-1.0	+2.5	High
453	+8.3	+6.4	High
447	+3.6	+5.1	High
458	+9.2	—	Low
420	+3.6	—	Low
448	+4.1	-2.2	Low
404	—	+2.6	Low
Average	+5.6	+2.6	

^a 16.2 b.v./h, 30 °C.

^b High = 0.11 to 0.16 mequiv./ml; low = 0.06 to 0.07 mequiv./ml

Table 1 gives the results. A correction of -0.7% has been added to the higher-temperature runs to allow for the expansion of water between 30 and 50 °C. Slower flow gave an average increase of 5.6% in amount of acid adsorption, higher temperature an increase of 2.6%. The effects of these variables, however, might be expected to show up more with influents of higher concentration. If runs with less-concentrated influents are omitted from the averages, the increase in acid adsorption goes up to 6.2% for slow-flow runs and 3.7% for high-temperature runs.

No pattern could be detected in effluent acid concentrations from these runs. They ranged from 12 to 86×10^{-5} mequiv./ml and averaged 41×10^{-5} . In all cases the decrease in acidity was over 99%; it averaged 99.6%. Reduction in phosphorus averaged 97.9% for the standard and slow-run flows, 98.6% for the 50 °C runs. Phosphorus data are given in Table 2; it can be seen that its concentration, in both influent and effluent, varies directly with the overall acidity of the influent.

Table 3 shows the effect of the anion-exchange process on c.o.d. and solids concentrations. Runs are listed in order of decreasing influent acidity. In runs two through four, acid adsorption proceeded at the standard flow-rate of 16.2 b.v./h. The flow-rate

TABLE 2. Effect of influent temperature and flow-rate on phosphorus removal

Phosphorus in influent (mg/l)	Standard runs, 16.2 b.v./h, 30 °C (mg/l)	Phosphorus in effluent Slow flow, 12.0 b.v./h (mg/l)	High temperature, 50 °C (mg/l)	Total acid in influent (mequiv./ml)
272	4.0	4.6	2.3	0.157
244	5.5	3.5	4.8	0.151
244	4.9	4.7	4.7	0.150
182	6.9	6.1	—	0.114
85	1.3	—	1.8	0.072
60	0.8	0.6	0	0.065
58	1.4	2.1	—	0.064

TABLE 3. Effect of anion exchange on c.o.d. and solids

Acidity of influent (mequiv./ml)	c.o.d.		Decrease in c.o.d. (%)	Solids		Decrease in solids (%)
	Influent (mg/l)	Effluent (mg/l)		Influent (%)	Effluent (%)	
0.156	11 210	7780	31	1.26	0.69	45
0.097 ^a	10 380	5520	47	0.95	0.43	54
0.097 ^a	10 380	5460	47	0.95	0.43	55
0.088	8640	4420	49	0.88	0.35	60
0.063	5270	3650	31	0.73	0.34	54
0.062	6330	3390	46	0.65	0.29	55
0.058	7030	4380	38	0.62	0.30	52

^a Two runs on the same influent.

TABLE 4. Effect of waste treatment on c.o.d., solids and reducing sugars

Treatment stage	c.o.d. (mg/l)	Decrease in c.o.d. (%)	Solids (%)	Decrease in solids (%)	Reducing sugars (%)
Untreated waste	23 710		2.48		0.17 ^a
After protein and amino-acid removal	9800	59	0.93	63	0.24
After anion removal	5130	48 ^b ; 78 ^c	0.40	57 ^b ; 84 ^c	0.19

^a Determined on deproteinised waste.^b Decrease produced by anion exchange.^c Overall decrease.

for the others was 12.0 b.v./h. For the three standard runs, data were also obtained for c.o.d., solids and reducing sugar concentrations in untreated waste and after amino-acid removal. Average values are given in Table 4. Anion-exchange resulted in a 48% decrease in c.o.d. and a 57% decrease in solids; decreases for the entire purification process (removal of protein, cation, amino acids, organic acids and phosphorus)

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were 78 and 84 %, respectively. Non-reducing sugars were absent in the waste after amino-acid removal—probably as a result of hydrolysis caused by the low pH of the waste (1.5 to 1.9) after cation-exchange. This hydrolysis may be reflected in the increase in reducing sugars shown in Table 4; the subsequent decrease in reducing sugars is unexplained.

3.2. Elution of acids

For the early runs, acids were eluted (as ammonium salts) with 780 ml of 1 N-NH₄OH—a little over 50 % in excess of the calculated column capacity. This also served to regenerate the free-base form of the resin. Flow-rate for this step and for the first bed

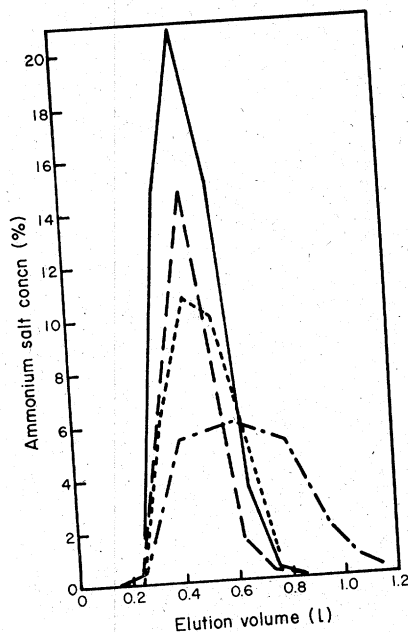


Figure 2. Effect of eluate recycling and NH₄OH strength on concentration of ammonium salts. —, 4.5 N-NH₄OH recycled; ---, 4 N-NH₄OH; ····, 2 N-NH₄OH; — · — ·, 1 N-NH₄OH.

volume of the following water-rinse (salts and NH₄OH still being eluted) was 3.6 b.v./h. For later runs, including those made for the influent flow-rate and temperature studies, the regenerant was 390 ml of 2 N-NH₄OH. The same low flow-rate was used for all regenerant concentrations.

In a study of conditions for obtaining the maximum concentration of salts, runs were made using 1 and 2 N-NH₄OH in the amounts given above. Runs were also made with 320 ml of 4 N-NH₄OH. After one 4-N run, 400 ml of that part of the eluate and rinse most concentrated in acids was mixed with 102 ml of concentrated NH₄OH—enough to make the solution approximately 4.5 N in free NH₄OH. Of this 320 ml was used as regenerant for the next run. This recycling was repeated three times. Eluate fractions were dried to constant weight to determine salt concentrations. Figure 2 shows typical curves for ammonium salt concentration at each regenerant strength

and the curve for the final recycling. Figure 3 graphs the progress of salt concentrations and the total weight of salts recovered for all the recyclings; it is apparent that after three recyclings the curves are beginning to level off. The curve for average concentration is stepped because the third point was determined on a larger volume of eluate than the second. Similar data for the non-recycled runs are given in Table 5. Going from 1 to 4 N-ammonia increased average salt concentration from 4.3 to 7.8%; recycling four times increased it to 11.1%. Although it would appear from Table 5 that regenerating above 4 N in strength might give even higher salt concentrations, the hazards of using strong ammonia must be considered. There is also an indication that at the higher NH_4OH concentrations the total amount of salts collected decreases somewhat.

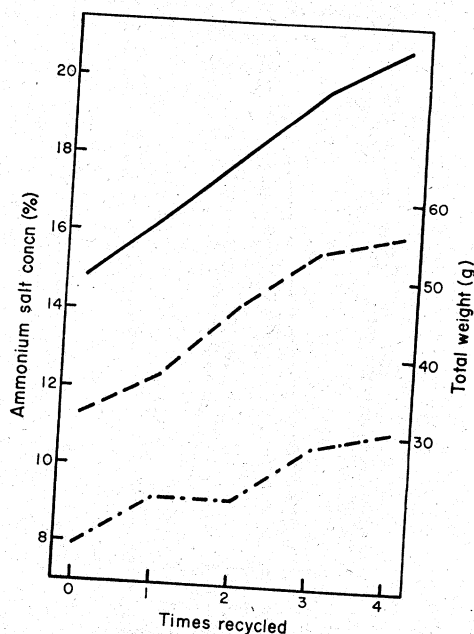


Figure 3. Effect of eluate recycling on concentration and weight of ammonium salts. —, Maximum concn; ---, total weight; - · -, average concn.

3.2.1. Composition of eluate

Analyses of eluates from two runs gave an average of 4% pyroglutamic acid, 12% malic acid, 57% citric acid, 6% phosphoric acid, 3% oxalic acid and 18% of unidentified acids. One eluate also contained about 1% aspartic acid. Relative amounts of acids are similar to those previously obtained for potato extracts¹¹ provided allowances are made for the nearly complete removal of glutamic and aspartic acids by the cation-exchange process. Pyroglutamic acid is probably an artifact derived from glutamic acid.

Although the unidentified acid came off the analytical anion-exchange column in one peak, paper chromatography revealed it to be a mixture of at least three or four components. The use of 3:1 acetone-25% CCl_3COOH as eluting solvent¹² produced

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two major spots with R_F 0.47 and 0.61. The elution volume of the material from the analytical column and the fact that it reduced the molybdate spray reagent of Hanes and Isherwood¹³ indicated it might contain organic phosphates such as sugar phosphates, nucleotides or phytic acid. Also, its infrared curve showed no carboxyl and only slight C-H absorption compared to the highly polar groups present; one broad band at 2900 to 3100 cm^{-1} could be OH on either phosphorus or sulphur. In spite of this, however, analysis of the material showed only 0.3% phosphorus and there was very little chromatographic evidence for the above phosphates. Some indication of the presence of nucleotides was the fact that a "beard" under the lower major spot gave a pale-brown colour reaction with *p*-anisidine spray reagent¹⁴ and absorbed light from a 254-nm lamp.

TABLE 5. Concentration and total weight of salts in NH_4OH eluates

NH_4OH concentration (normality)	Salt concentration Average ^a (%)	Maximum (%)	Total weight of salts ^a (g)	Volume of eluate ^b (ml)
1	4.0	6.7	37.7	950 ^c
1	4.5	6.0	36.0	800
2	—	11.5	—	—
2	—	10.9	—	—
2	6.8	10.8	34.2	500
2	6.0	10.5	30.2	500
4	7.7	14.0	31.0	400
4	7.9	15.4	31.6	400
4	7.9	14.8	31.4	400

^a In the volume of eluate given in the last column.

^b 100-ml fractions. Includes only fractions containing at least 0.5% salts.

^c Major fractions 200 ml.

In addition to the non-volatile acids determined the eluate must contain sulphite, since NaHSO_3 had been added in preparing the original waste-water so that recovered products would be light-coloured. Anion-exchange influents were estimated to contain about 0.007 mequiv./ml of sulphite. It is possible that the unidentified material may consist in part of artifacts produced by sulphite reactions—but not in entirety, since analyses of acids in unsulphited potato extracts also show an unidentified peak.

3.3. Rinse procedures

For standard runs, the water-rinse after acid adsorption consisted of a 120-ml downwash (to clear piping), a 2-l backwash at 75% bed expansion and then a drainage of 140 ml to reduce the head of water. Elution of acids was followed by a 2-l downwash (at 12.0 b.v./h after the first bed volume). These relatively large volumes of water were used to insure that impurities did not accumulate on the column during the various studies. In some runs the backwash was reduced to 634 ml (2 b.v.) and the final downwash to 951 ml (3 b.v.); this did not affect the column capacity.

3.4. Commercial possibilities

For plant operation, a three-column, continuous operation system could be set up such as previously described for amino-acid removal.⁶ In this system, while one column is being loaded, a second is acting as scavenger to reduce acid leakage and the third is being eluted. If it is assumed as before⁶ that the plant produces 6760 gal^a/hr of waste, each column would require a bed of 417 gal (55.7 ft^{3b}) of resin to achieve the 16.2 b.v./h flow-rate of the standard laboratory runs. If the slower rate (12.0 b.v./h) is desired, 562 gal (75.1 ft³) would be needed.

The acid mixture recovered from the wastewater was tested as a replacement for phosphate detergent builders after first removing excess NH_4OH from the eluate and converting to sodium salts by passing through a cation-exchange resin in the sodium form. A few drops of hydrogen peroxide were added to decolorize the solution and prevent turbidity which otherwise formed on standing. Its pH was adjusted to 7.0 and portions were tested with four different detergents. With three of these, the solution performed about as well as the control phosphate builder in washing ability, but there was considerable soil redeposition on clean test-swatches. When the solution was first adjusted to pH 10, a pH at which detergents are usually more effective, there was improved washing ability with only one of the detergents and there was still redeposition of soil in spite of the addition of carboxymethylcellulose as a suspending agent. A further difficulty at pH 10 was the fact that the pH of the solution decreased on standing. This may have been caused by alkaline hydrolysis of the unidentified material.

For testing as a detergent builder or for other uses such as food uses, it may be better to obtain individual acids or more restricted mixtures, such as a mixture of citric and malic acids. This could be done by using a volatile acid to elute the potato acids from the column in a manner similar to that used for determining the individual acids.⁷ However, this would introduce an extra step in the process, since the resin would still have to be eluted with ammonia to restore it to the free-base form.

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^a Throughout this paper 1 gal \approx 3.79 l.

^b Throughout this paper 1 ft³ \approx 0.0283 m³.

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